

Voltammetric and Emf Measurements on the Nickel-Nickel(II)
Couple in Molten Fluorides*

D. L. Manning, Gleb Mamantov,** H. W. Jenkins**

Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee and

**Chemistry Department, University of Tennessee,
Knoxville, Tennessee

Extensive electrochemical investigations have been reported for molten salt systems in recent years.⁽¹⁻⁵⁾ From such work, valuable insight has been gained into the behavior of electroactive constituents in molten chloride and nitrate systems, and to a lesser degree, sulfate and phosphate melts. It appears that the electrochemistry of molten fluorides has been investigated least of all. The most probable reason for this lack of interest is the inability to use (on a long term basis) glass or quartz as insulators and container materials.

Interest in molten fluorides has increased immensely at the Oak Ridge National Laboratory due to their application as reactor fuels. As a result, considerable research is being conducted to characterize to a greater extent this class of molten salt systems. We are engaged in electroanalytical measurements in molten fluorides with the hope of adapting such techniques to in-line methods of analysis; this paper is concerned with the application of controlled-potential voltammetry and Emf measurements to the study of the Ni/Ni²⁺ couple in molten LiF-NaF-KF (46.5-11.5-42 mole %) and LiF-BeF₂-ZrF₄ (65.6-29.4-5.0 mole %). Nickel is usually encountered in molten fluorides as a corrosion product.

For the controlled-potential voltammetric studies, the molten fluoride, ~40 ml volume, is contained in a graphite cell (~2" dia x 4" long) which is then enclosed in a quartz jacket to maintain a vacuum or controlled atmosphere. The stationary dip type electrodes are inserted into the melt through the Swagelok compression fittings which are located on the cap of the quartz enclosure. To isolate the counter electrode, it is inserted into a porous graphite or thin walled boron nitride inner compartment of the cell. Usually the melt is maintained in an inert atmosphere. Provisions are made, however, to evacuate the cell whenever necessary. Disassembly of the cell, salt additions, etc. are always performed in a dry box.

A controlled-potential voltammeter, ORNL Model Q-1988, modified to measure cell currents to 5 milliamperes and to produce rates of voltage scan from 0.05 to 10 volts per minute was used for the voltammetric measurements. The potential of the pyrolytic graphite indicator electrode is measured versus a platinum quasi-reference electrode because at the time of the voltammetric work we did not have a practical reference electrode for molten fluoride systems.

In high-temperature melts, the transport process to the electrode is governed by both diffusion and convection. Convection is predominant at relatively slow scan rates (~50 m.v. per min.) with the result that the current-voltage curves at stationary electrodes are s-shaped. Such curves are analytically useful, however, because the limiting current is usually proportional to the concentration of electroactive species, but they are difficult or impossible to interpret theoretically.

To minimize convection and achieve conditions where diffusion is predominant, the current-voltage curves were recorded at scan rates of 1 to 10 volts per minute. Such curves are shown in Figure 1; in general, peak-shaped curves were obtained.

The equation for the peak current, i_p , for the reversible deposition of an insoluble substance at 500°C is $i_p = 2.28 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2}$ where i_p is peak current, μa , n - electron change, A - electrode area, cm^2 , D - diffusion coefficient, C - concentration of diffusion species, mM and v is voltage scan, volts per sec. Plots of i_p versus $v^{1/2}$ for nickel were linear at temperatures of 500, 570 and 600°C. The diffusion coefficient as calculated from the slope of the line at 500°C is approximately $1 \times 10^{-6} cm^2/sec$. From plots of $\log D$ vs $1/T$, and the equation

$\log D = -E/2.3 RT + \log A$, an activation energy (E) of about 18 k cal/mole was calculated for the reduction of nickel in molten LiF-NaF-KF.

The analytical utility of the voltammetric approach to the determination of nickel in the molten state was demonstrated from the linear dependence of i_p on nickel concentration over the range studied, i.e. approximately 10 to 80 ppm.

Electromotive force measurements were carried out on the Ni/Ni²⁺ couple in concentration type cells in molten fluorides to check for Nernstian reversibility and to ascertain the feasibility of utilizing the Ni/Ni²⁺ couple as a high-temperature reference electrode for fluoride systems. The approach is similar in principle to utilization by Laitinen and Liu⁽⁴⁾ of the Pt/Pt²⁺ couple as a reference electrode in molten chlorides.

The apparatus used to contain the melt is shown in Figure 2. Essentially it is a small vacuum dry box (24" long, 20" deep and 15" high) which is outfitted with a furnace, vacuum and controlled atmosphere facilities and a moisture monitor. Utmost care is exercised to protect the molten fluorides from moisture contamination because of the affinity of the molten fluorides to moisture and the resultant precipitation of oxides. A schematic diagram of the cell and furnace assembly is shown in Figure 3. The melt (~400 ml) is contained in a graphite cell. A spiral nickel electrode, platinum stirrer, Pt-10% Rh thermocouple and the inner electrode compartment are positioned in the melt. The inner compartment of the cell is shown in Figure 4. It consists of a thin-walled boron nitride compartment which contains the same fluoride melt and a fixed concentration of dissolved NiF₂. A nickel electrode is inserted into this compartment. Hot pressed boron nitride is an insulator in molten fluorides but is slowly penetrated by them. As a result of this effect, BN can be utilized to separate the two half-cells and yet achieve electrical contact because such contact is made when the BN becomes wetted by the melt. For molten LiF-NaF-KF, penetration of the BN (1/32" wall thickness) occurs within a day or so; however, it is much slower for LiF-BeF₂-ZrF₄ melts. Approximately a week is required for the resistance through the BN to drop to ~1000 ohms or less.

With stirring, weighed portions of NiF₂ were added to the melt. After each addition, measurements were made and a sample withdrawn for nickel analysis. From the equation $\Delta E = RT/2.3 nF \log X_1/X_2$ and plots of ΔE versus $\log X_{Ni}$, as shown in Figure 5, it was demonstrated that the nickel system exhibits reasonable Nernstian behavior at 500°C. The concentration of nickel varied from approximately 10⁻⁵ to 10⁻³ mole fraction. From the standpoint of Nernstian reversibility, the nickel couple appears to be a good choice for a reference electrode in molten fluorides.

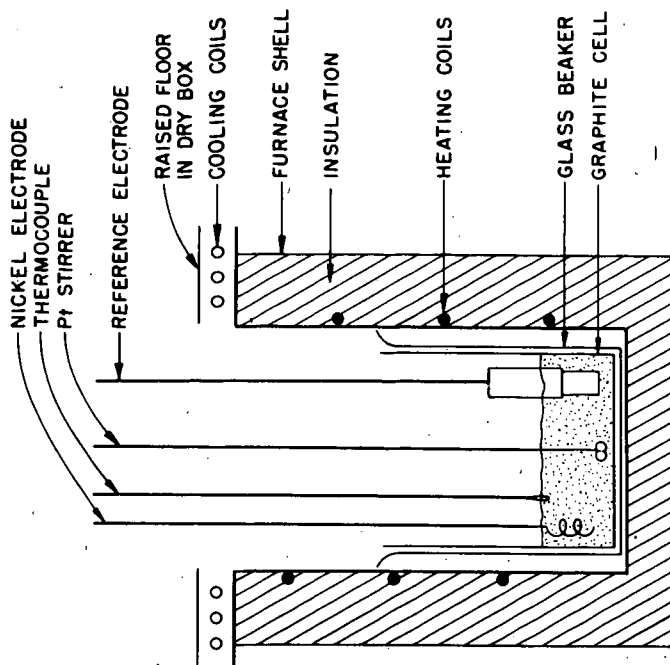
Stability studies conducted so far are encouraging. For a run in molten LiF-NaF-KF, the Emf remained constant to within ± 2 mv over a two-week period. These studies are continuing and longer stability tests are planned.

References

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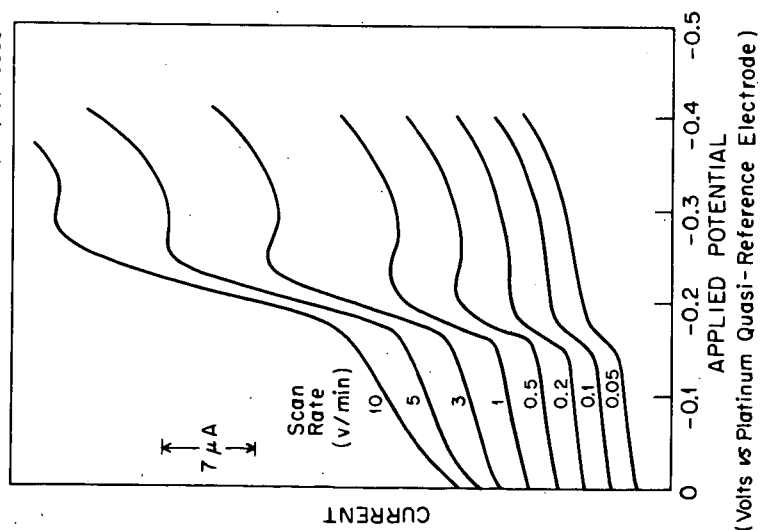
ORNL - DWG. 66-11928



Furnace and Cell Assembly.

Fig. 3

ORNL - DWG. 63-8003



Effect of Scan Rate on the Current-Voltage Curves for Nickel
LiF-NaF-KF, 500°C
Nickel, 23 ppm

Fig. 1

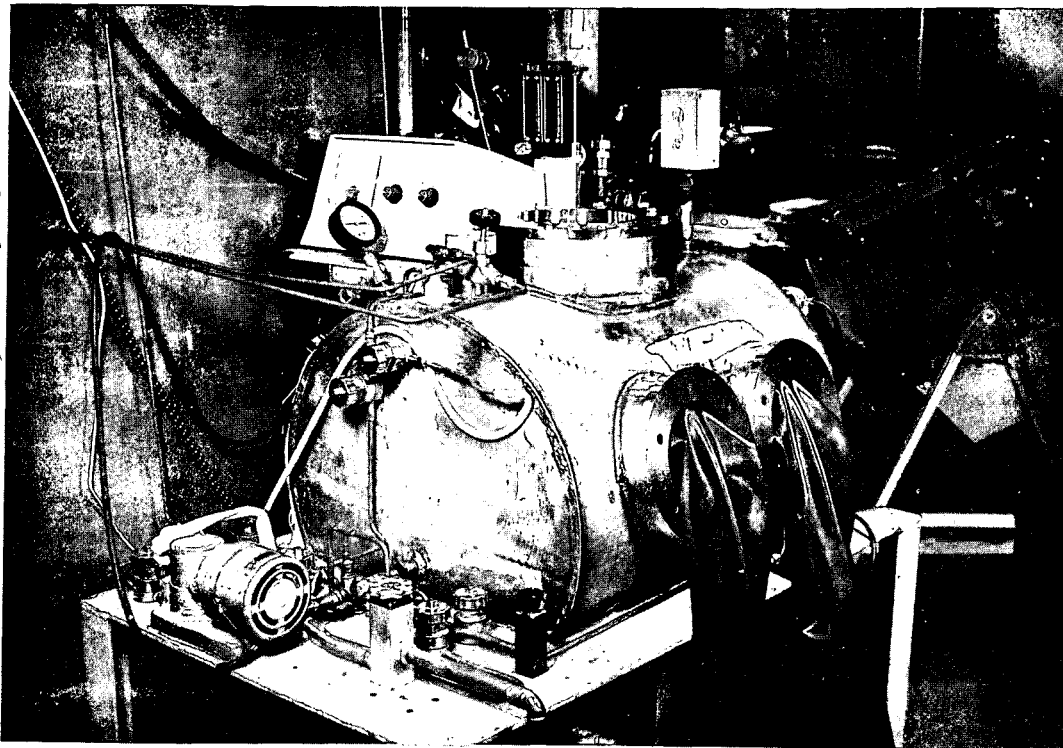
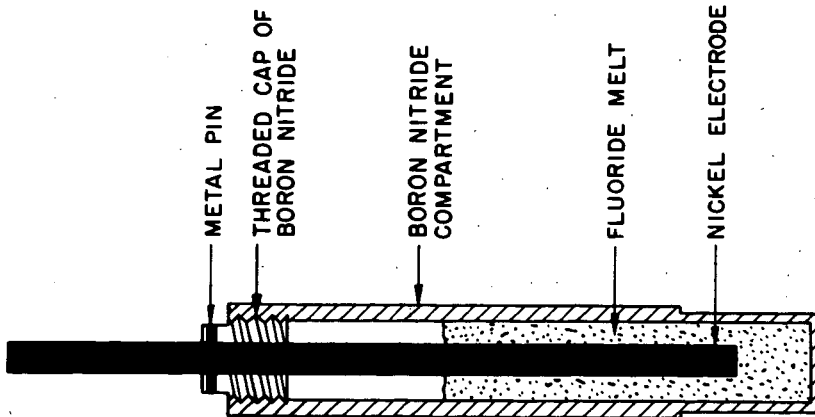
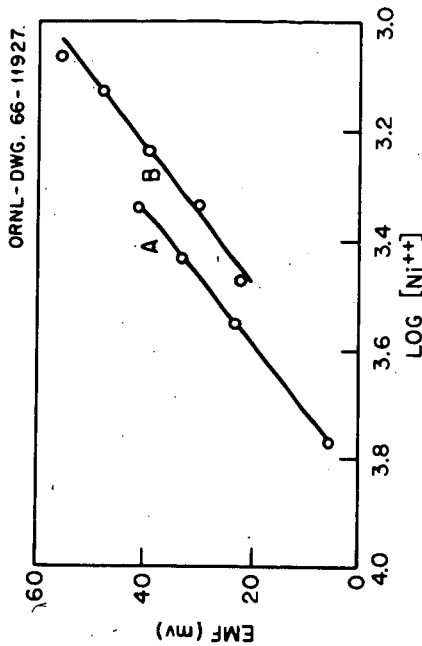


Fig. 2. Dry Box-Furnace Combination for Containing Fluoride Melts.



Nickel Electrode in Boron Nitride.



Nernstian Log Plots for Ni/Ni^{+2} Couple in Molten Fluorides.

(A) LiF-NaF-KF (517°C) Slope 0.080; Theo. 0.078.

(B) $\text{LiF-BeF}_2\text{-ZrF}_4$ (507°C) Slope 0.081; Theo. 0.077.

Fig. 5